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**(71) Applicant** *(for all designated States except US)*: SURFACE TECHNOLOGY SYSTEMS LIMITED [GB/GB]; Imperial Park, Newport, Gwent NP1 9UJ (GB).

**(72) Inventors; and**
**(75) Inventors/Applicants** *(for US only)*: BHARDWAJ, Jyoti, Kiron [GB/GB]; 60 Campion Drive, Bristol BS12 0BH (GB). LEA, Leslie, Michael [GB/GB]; Hideaway, 16B New Road, East Hagbourne, Didcot, OX11 9JH (GB). SHEPHERD, Nicholas [GB/GB]; 2 Clancaiach Road, Whitchurch, Cardiff CF14 1PX (GB).

**(74) Agents:** JAMES, Michael, John, Gwynne et al.; Wynne-Jones Laine & James, 22 Rodney Road, Cheltenham, Gloucestershire GL50 1JJ (GB).

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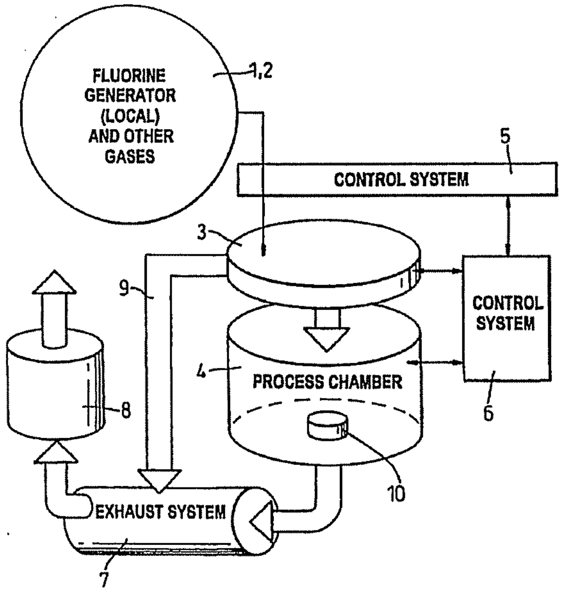
**Published**
*With international search report.*

**(54) Title:** GAS DELIVERY SYSTEM




**(57) Abstract**

A substrate is treated by supplying an etchant and/or deposition gas into a chamber (4) in which the substrate is situated. In order to avoid the problems associated with transportation of toxic gases, the gases required for such processes are delivered directly from a delivery system (1, 2, 3) positioned locally to the chamber.

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"Gas Delivery System"

This invention relates to a gas delivery system, particularly, although not exclusively, one for use in dry processing apparatus, for example one in which a switched etch/deposition cycle or continuous process is used on a semiconductor wafer or the like.

Continuous plasma processes as well as switched etch/deposition processes use sulphur hexafluoride as the standard etch chemistry. The industry demands for higher etch rate processes have led to the investigation of alternative process etch gases which allow an increase in the density of active species in the process chamber resulting in improved process rates.

Several different chemistries are known to be likely candidates to enhance the process rate. All suffer from increased cost, greater health and safety risks and poor commercial availability. These factors combine to make the economics of implementing these chemistries extreme and/or the installation too hazardous. Latterly, a number of molten electrolyte gas generators have been reported and are just being made commercially available. Generation of gases by this means includes fluorine, nitrogen trifluoride and chlorotrifluoride. An example is a fluorine gas generator cell as described in US Patent No. 5688384. The generators are able to generate the process gases to high purity and at a reasonable cost and risk. The gas generators contain a solid when cold and this allows for

safe transportation and storage of the units.

The incorporation of these gas generators into a gas delivery system local to the process chamber allows a novel capability to introduce different processes gases into a variety of process schedules to achieve a process advantage. There are many novel aspects to the application of these gas generators to a dry processing environment in terms of system design, gas delivery control, system transportation, ease of installation and process advantages.

Thus, according to a first aspect of the present invention there is provided an apparatus for treating a substrate, the apparatus comprising a chamber, a support for a substrate and a delivery system for delivering an etchant and/or a deposition gas into the chamber, wherein the delivery system is positioned locally to the chamber.

"Locally" (or point of use) means that the delivery system is located near to a process chamber or a number of chambers or number of systems near to one another, so that the gases created can be delivered directly to the chamber or system for immediate use rather than being created off-site and transported in a suitable container for subsequent introduction into the apparatus.

The delivery system will preferably include a molten electrolyte gas generator

According to a second aspect of the present invention, there is provided a method of treating a substrate

comprising providing an etchant and/or deposition gas to a chamber in which the substrate is situated, wherein the gas is delivered from a delivery system positioned locally to the chamber.

According to a third aspect of the present invention, there is provided a method of treating a substrate comprising cyclically performing the following steps:

a) etching the substrate with a gas;

b) depositing a passivation layer on the surface of an etched feature; and

c) selectively removing the passivation layer from the base of the etched feature,

wherein the etchant gas comprises fluorine, nitrogen trifluoride or chlorotrifluoride or mixtures thereof generated locally.

If desired such gases can be mixed with $SF_6$ or other known etchant gases.

Ideally, in the methods of the invention as defined above, the gases are supplied from a delivery system including a molten electrolyte gas generator.

Safety issues compared to the conventional cylinder delivery:

1. The generators operate at or near atmospheric pressure eliminating the need for high pressure regulators on the system.

2. There is no potentially hazardous gas in the system until the user demands production eliminating hazardous

storage problems. The risks to operators are significantly reduced.

3. At room temperature the gas generators have a solid constitution eliminating the risks of transporting the hazardous gas on site or to the working location.

4. The local delivery on demand eliminates long gas lines from a central store on the installation and the associated risks of hazardous gases in these pipes.

Reduced cost of installations of the gas generators compared to conventional cylinder delivery.

1. The local delivery system eliminates the expense to add additional long gas lines from a central store on the installation to the processing environment.

2. The production and quality of the process gas from the generator is typically comparable to that produced by the high pressure cylinders.

3. The close proximity to the process equipment minimises the safety precautions needed to protect the operator during any maintenance operations.

Features of this novel use and design of the gas generators may be:

1. A totally dry method of heating the electrolyte instead of the normal hot water bath.

2. The gas generators produce a gas at both the anode and the cathode of the electrolytic cell. The two gases are potentially extremely reactive but are separated by the design of the system to avoid any possible recombination.

3. The gas generators are only designed to be operated at or near atmospheric pressure. The design of the gas line to the process chamber incorporates a novel control system such that the generator does not see the low pressure (vacuum) at the process chamber. This is an important design feature of the gas generators operation on the overall system.

4. Included in the local delivery system is the ability to polish the generated gas to remove unwanted impurities before passing into the process chamber.

It is envisaged that the invention can be used in our following co-pending applications:

1. Continuous operation dry processing (European Patent Application No. 9909091.3). The gas generator can be used to supply a process gas to etch substrates placed in the process chamber. This may involve the use of a plasma to generate the reactive species or without a plasma where the generated gas reacts spontaneously with the substrate.

2. Alternative gas for the switched plasma process (EP-A-0822584 and EP-A-0822582). The addition of the generated gas allows the replacement or addition to the existing process etch gas used in the switched plasma process. The generated gas e.g. fluorine, nitrogen trifluoride or chlorotrifluoride can be advantageously used to enhance the process etch rate either individually or in combination with the existing sulphur hexafluoride.

3. Alternative gas for the plasma-less switched process

(International Patent Application No. PCT/GB99/02368). Where the generated gas spontaneously reacts with the substrate, substitution of the sulphur hexafluoride process gas will also allow the operation of the process without plasma in the process chamber.

In addition, it is envisaged that the invention can be used in the generation of gases for a plasma/plasma-less switched process similar to that in International Patent Application No. PCT/GB99/02368. The ability to generate gases or combine gas mixtures which either require a plasma to produce the reactive species or spontaneously react with the substrate, allows the capability to introduce a process schedule which may only require a plasma for one or other the process steps in the overall process schedule.

The invention may be performed in various ways and preferred embodiments thereof will now be described, by way of example, with reference to the accompanying Figure 1 comprising a diagrammatic illustration of a general gas generation system of this invention.

In the arrangement shown in Figure 1, one or more precursor gases are passed from one or more suitable supply source(s) 1, 2 to a process chamber 4 where a dry process utilising that gas is to take place. Appropriate valving will include one or more valves provided at 3 for appropriate control and isolation means. Linked control systems 5 and 6 monitor and maintain the required gas supply to either the process chamber 4 or to the bypass

line 9.

From the process chamber 4 gases pass to an exhaust system 7, which in turn leads to an abatement tool 8 (which is usually needed). The bypass outlet 9 leads from the reaction chamber 3 to the exhaust system, whereby gases can be switched into the process chamber only when required for processing. This also allows the means for ensuring stable gas composition and flow to be maintained prior to switching into the process chamber. Within the process chamber 4 there is a support 10 for a substrate which is to be treated by the supplied gas(es).

## CLAIMS

1. An apparatus for treating a substrate, the apparatus comprising a chamber, a support for a substrate and a delivery system for delivering an etchant and/or a deposition gas into the chamber, wherein the delivery system is positioned locally to the chamber.

2. An apparatus according to claim 1, wherein the delivery system includes a molten electrolyte gas generator.

3. A method of treating a substrate comprising cyclically performing the following steps:

a) etching the substrate with a gas;

b) depositing a passivation layer on the surface of an etched feature; and

c) selectively removing the passivation layer from the base of the etched feature,

wherein the etchant gas comprises fluorine, nitrogen trifluoride or chlorotrifluoride or mixtures thereof generated locally.

4. A method according to Claim 3, wherein said etchant gas is mixed with $SF_6$ or other known etchant gases.

5. A method according to claim 3 or claim 4, wherein the gases are supplied from a delivery system including a molten electrolyte gas generator.

6. Any novel combination of features of apparatus or method for treating a substrate and substantially as herein described and/or illustrated in the accompanying drawing.

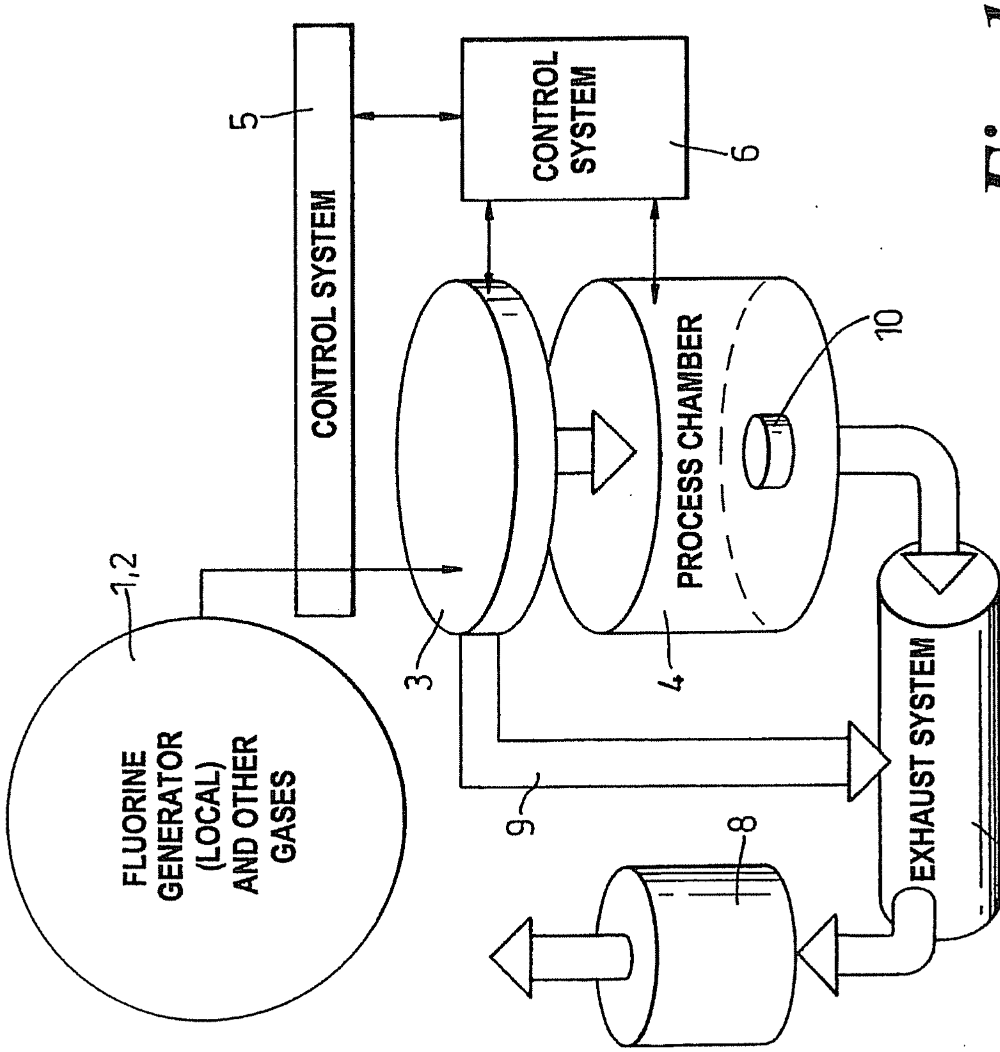
CONTROL SYSTEM
5
CONTROL SYSTEM
6
PROCESS CHAMBER
10
1,2
FLUORINE GENERATOR (LOCAL) AND OTHER GASES
3
4
EXHAUST SYSTEM
7
8
9

*Fig. 1*

# INTERNATIONAL SEARCH REPORT

In ational Application No
PCT/GB 00/00789

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 H01L21/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0 429 809 A (TEXAS INSTRUMENTS)<br>5 June 1991 (1991-06-05)<br>abstract; figures 1,2<br>page 2, line 51 -page 3, line 2<br>page 4, line 30-32 | 1,4,5 |
| X | WO 99 03137 A (APPLIED MATERIALS)<br>21 January 1999 (1999-01-21)<br>abstract; figure 3<br>page 3, line 24 -page 4, line 6 | 1,4 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 29 May 2000 | 09.06.00 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
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# INTERNATIONAL SEARCH REPORT

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 7
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see rule 6.2 a (PCT)

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

Continuation of Box I.2

Claims Nos.: 7

see rule 6.2 a (PCT)

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 00/00789

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0429809 A | 05-06-1991 | US 5002632 A | 26-03-1991 |
| | | JP 3194930 A | 26-08-1991 |
| WO 9903137 A | 21-01-1999 | EP 0996966 A | 03-05-2000 |